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(54) [Title of the Invention] RECYCLABLE LAMINATE AND PRINTED CIRCUIT BOARD USING IT

(57) [Abstract]

[Object] The object of the present invention is to provide a laminate and a printed circuit board which are recyclable and have good heat resistance.

[Structure] A recyclable laminate consisting of an electrically insulating layer and an electrically conductive layer, wherein a synthetic resin soluble in a solvent and having a glass transition temperature of no less than 260°C is used as a synthetic resin component of the electrically insulating layer. A printed circuit board using the laminate. Examples of synthetic resin include polyimides and fluorinated polyimides, in particular, polyimides using 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl as a diamine component.

[Effect] Recyclability makes it possible to protect environment and conserve natural resources.

[Patent Claims]

[Claim 1] A recyclable laminate consisting of an electrically insulating layer and an electrically conductive layer, wherein a synthetic resin soluble in a solvent and having a glass transition temperature of no less than 260°C is used as a synthetic resin component of the electrically insulating layer.

[Claim 2] The recyclable laminate as described in Claim 1, wherein a polyamide soluble in a solvent and having a glass transition temperature of no less than 260°C is used as the synthetic resin.

[Claim 3] The recyclable laminate as described in Claim 1, wherein a fluorinated polyamide soluble in a solvent and having a glass transition temperature of no less than 260°C is used as the synthetic resin.

[Claim 4] The recyclable laminate as described in Claim 1, wherein a solvent-soluble polyimide, polyimide copolymer, or polyimide blend prepared by using a fluorinated diamine represented by the following structural formula (Formula 1)

(Formula 1)

...

is one of synthetic starting materials.

[Claim 5] A printed circuit board employing the recyclable laminate described in Claim 1.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Utilization] The present invention relates to a recyclable laminate having excellent heat resistance, and to a printed circuit board.

[0002]

[Prior Art Technology] From the standpoint of wiring structure, printed circuit boards can be classified into single-side sheets, two-side sheets, and multilayer sheets. They are manufactured mainly from copper-clad laminates. Copper-clad phenolic resin laminates with paper substrates, copper-clad epoxy resin laminates with paper substrates, copper-clad epoxy resin laminates with glass substrates, and copper-clad polyimide laminates have been used as the above-mentioned copper-clad laminates. Furthermore, laminates using a fluoropolymer have recently been also manufactured as laminates with a low dielectric constant for high-frequency applications. Heat resistance, dimensional stability, low dielectric constant, and low cost have been traditionally considered as main criteria in selecting synthetic resins for laminates and printed circuit boards.

In future, however, other criteria will apparently become important. Thus, recyclability is a criterion dictated by environmental concerns and shortage of natural resources. From the standpoint of this criterion, phenolic resins, epoxy resins, thermosetting polyimides, and fluoropolymers that have been used in prior art are difficult to recycle because they are insoluble in solvents and cannot be melted even by heating. Moreover, waste containing such plastics is difficult to process. By contrast, thermoplastic polyimides such as polyetherimides can be melted by heating and are soluble in solvents. Therefore, they can be recycled. However, their glass transition temperature is less than 260°C and they have insufficient heat resistance.

[0003]

[Problems Addressed by the Present Invention] The present invention was developed to resolve the above-described problems and its object is to provide a laminate and a printed circuit board which have good heat resistance in soldering and can be recycled.

[0004]

[Means to Resolve the Problem] The essence of the present invention is briefly described above. The first present invention provides a laminate consisting of an electrically insulating layer and an electrically conductive layer, wherein a synthetic resin soluble in a solvent and having a glass transition temperature of no less than 260°C is used as a synthetic resin component of the electrically insulating layer. The second present invention provides a printed circuit board manufactured from a laminate consisting of an electrically insulating layer and an electrically conductive layer, wherein a synthetic resin soluble in a solvent and having a glass transition temperature of no less than 260°C is used as a synthetic resin component of the electrically insulating layer.

[0005] The inventors have conducted an intensive study aimed at the resolution of the above-described problems. The results of this study laid the foundation for the present invention.

[0006] Examples of the electrically conductive layer employed in accordance with the present invention include sheets or foils of copper, aluminum, nickel, silver, gold and the like. It is especially preferred that a copper foil be used.

[0007] The synthetic resin employed in accordance with the present invention can be any resin which has a glass transition temperature of no less than 260°C, can be dissolved in a solvent and has good recyclability. Examples of suitable resins include polyesterimides, polyamidoimides, polyimides, and fluorinated polyimides of certain types. The especially preferred among them are polyimides, polyimide copolymers, or polyimide blends prepared by using a fluorinated diamine represented by the following structural formula (Formula 1) as a synthetic starting material.

[0008]

(Formula 1)

[0009] A polyamide acid which is a precursor for those fluorinated polyimides can be manufactured under the same conditions as those employed for the manufacture of ordinary polyamide acids. Thus, the reaction of the above-described fluorinated diamine with a tetracarboxylic acid component is usually conducted in a polar organic solvent such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide (DMAc), N,N-dimethylformamide and the like. In accordance with the present invention, diamines and tetracarboxylic acid components are not necessarily used together as individual compounds. Thus, several diamines and tetracarboxylic acid components can be used in a mixture. In such a case, the total number of moles of one or several diamines should be equal or almost equal to the total number of moles of one or several tetracarboxylic acid component. Furthermore, in order to manufacture a polyimide solution from a polyamide acid solution, the polyamide acid solution can be heated at a temperature of 150-200°C.

[0010] Prepregs prepared by impregnating a substrate with a synthetic resin can be used as the electrically insulating layer employed in accordance with the present invention. The synthetic resin can be used alone, or a filler can be added thereto.

[0011] Any substrate that have been ordinary used for laminated materials can be used in accordance with the present invention. Examples of suitable substrates include various glass cloth and sheets, for example, D glass, S glass, and E glass containing SiO_2, Al_2O_3 and the like, and Q glass using quartz. Examples of suitable fillers include powdered alumina, silica, beryllia, boron nitride and the like.

[0012] A laminate is obtained by employing prepregs containing the synthetic resin, laminating the required number of prepregs on one or both sides of a metal sheet, then placing a copper foil as an outer layer, heating, and pressing. The obtained laminate can be used to manufacture a printed circuit board by the ordinary method for the manufacture of circuit boards.

[0013]

[Embodiments] The present invention will be described below in greater detail based on embodiments thereof which, however, place no limitation on the present invention.

[0014] Embodiment 1

A total of 4.442 g of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, 3.202 g of 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl represented by Formula 1 above, and 40 g of N-methyl-2-pyrrolidone were placed in a triangular flask. The components were stirred for 48 h in a dry nitrogen flow at room temperature and then stirred under heating for 3 h at a temperature of 180°C to conduct imidazation. When the resulting polyimide solution was dropwise added to water, a white solid matter has precipitated. The polyimide solid matter was dissolved in ethyl acetate to obtain a polyimide solution. The polyimide solution was infiltrated into a glass cloth serving as a reinforcing material and dried for 30 min at a temperature of 150°C to obtain a prepreg. Copper foils were placed on the top and bottom of ten such prepregs, and the stack was press molded (pressure : 40 kgf/cm^2, temperature : 350°C, time : 2 h) to obtain a copper-clad laminate. The copper-clad laminate was allowed to stay for 1 day in an oven at a temperature of

300°C. The laminate was then inspected. No abnormalities were observed. Thermal properties of the employed polyimide were measured. The glass transition temperature of the polyimide was 335°C. The copper-clad laminate was then immersed in N-methyl-2-pyrrolidone and heated for 3 h at a temperature of 100°C. As a result, the polyimide was dissolved and the glass cloth and copper foil were separated. The N-methyl-2-pyrrolidone solution of polyimide was dropwise added to water and the polyimide solid matter could be recovered. A copper-clad laminate could be manufactured by the same method as described above by using the recovered polyimide solid matter.

[0015] Embodiment 2

A copper-clad laminate was obtained by the same operations as described above, except that 3.998 g of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane and 0.218 g of anhydrous pyromellitic acid dianhydride were added instead of 4.442 g of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride employed in Embodiment 1. The copper-clad laminate was allowed to stay for 1 day in an oven at a temperature of 300°C. The laminate was then inspected. No abnormalities were observed. Thermal properties of the employed polyimide were measured. The glass transition temperature of the polyimide was 343°C. The copper-clad laminate was then immersed in N-methyl-2-pyrrolidone and heated for 3 h at a temperature of 100°C. As a result, the polyimide was dissolved and the glass cloth and copper foil were separated. The N-methyl-2-pyrrolidone solution of polyimide was dropwise added to water and the polyimide solid matter could be recovered. A copper-clad laminate could be manufactured by the same method as described above by using the recovered polyimide solid matter.

[0016] Embodiment 3

A printed circuit board was fabricated by the usually employed subtract method by using the laminate fabricated in Embodiment 1. First, holes for aligning the printed pattern were made in the copper-clad laminate. Then, an etching resist was printed on the front surface, followed by printing the etching resist on the back surface. Etching was conducted, and then the etching resist was peeled off to form a circuit. As a result, a non-through-hole two-sided printed circuit board was fabricated. When the fabricated printed circuit board was immersed in N-methyl-2-pyrrolidone and heated for 3 h at a temperature of 100°C, the polyimide was dissolved and the glass cloth and copper foil were separated. The N-methyl-2-pyrrolidone solution of polyimide was dropwise added to water and the polyimide solid matter could be recovered.

[0017]

[Effect of the Invention] As described above, the laminate and printed circuit board in accordance with the present invention have good heat resistance in soldering and can be recycled. Therefore, they make a contribution to protection of environment and conservation of natural resources.